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CANADIAN PATENT

METHOD FOR PRODUCING PENTITOLS AND HEXITOLS

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The inv ntion relates to a method of producing pentitols and hexitols from wood.

According to the invention, wood, for instance in the form of sawdust, is first treated in a so-called prehydrolysis step at a temperature of about 15 to 30°C with hydrochloric acid of about 29 to 37 % concentration, whereby the concentration depends on the nature of the starting material. In this prehydrolysis step, the hemicelluloses and pentoses are dissolved. The obtained solution is freed from the hydrochloric acid, and if the starting material was rich in pentoses, xylose may be recovered from said solution in crystalline form.

The solid residue from the prehydrolysis step is then subjected at the ambient temperature of about 15 - 30°C to the main hydrolysis with strong hydrochloric acid of 39 - 42 % HCl, and this acidic solution is then worked up to a sugar solution from which the major part of the glucose content is recovered by crystallization.

The mother liquors from the glucose crystallization (main hydrolysis) and from the xylose crystallization (prehydrolysis), or the entire deacidified and purified prehydrolysis liquor itself, comprise mixtures of pentoses and hexoses which cannot be separated by crystallization, even when they are obtained relatively free of decomposition and polymerization products. These by-products of the wood saccharification are, therefore, of little economic value.

An economic separation and utilization of the by-product sugars of the wood saccharification is, however, possible by hydrogenation of the residual sugar syrups to polyols and by separation of said polyols.

The hydrogenation is preferably carried out in aqu ous

or methanolic solution in the presence of a catalyst under pressure and at elevated temperature. Suitable catalysts are nickel and/or copper, preferably in combination with other metals such as manganese or chromium. It is of advantage to hydrogenate at relatively low temperatures, for instance in the range of about 70 to 120°C, in order to avoid side reactions.

From the hydrogenated product, the pentitols are distilled off under mild conditions, for instance by removing first the solvent and then subjecting the product to steam distillation in vacuo. The obtained pentitols, particularly xylitol, are useful as plasticizers or softeners in the paper and tobacco industry or for cellulose ester films; they may also be employed as polyol component in the manufacture of alkyd type resins. Xylitol is also useful as sweetening agent in the food industry.

The distillation residue consists of hexitols, the composition of which depends to a certain extent on the nature of the starting material. Syrups obtained in the saccharification of softwood produce, on hydrogenation, relatively large amounts of mannitol, which may be recovered in pure crystalline form on concentration of the hexitol solution. The remaining hexitol solution consists essentially of sorbitol, which, after purification and concentration to syrup consistency may be used as plasticizer and humidifier.

The invention will be illustrated by the following examples, where parts are given by weight.

EXAMPLE 1

1,000 kg of pine wood comminuted to a grain size of about 1 mm were subjected to a prehydrolysis with 35 % HCl at a temperature of about 20 C, whereby 240 kg of hemicelluloses were dissolved. Subsequently, the material was subjected at the same temperature to the main hydrolysis step, whereby about 300 kg of cellulose were dissolved. Each of the hydrolysates was concentrated in vacuo to a thick syrup which contained about 3.5 % of residual hydrochloric acid, calculated on the sugar. Each of said syrups was diluted to a sugar content of about 15 per cent and heated in an autoclave for a period of three hours at 120 C. Subsequently, Fuller's earth was added for clarification and precipitation of small amounts of colloidal substances. The solutions were filtered and then passed through a bed of a decolorizing resin. The thus obtained liquids passed through an anion exchange resin in order to remove all free acids, comprising essentially hydrochlorid acid and small amounts of organic acids such as levulinic acid. Subsequently, the solutions passed through a cation exchange resin to remove all cations originated from the wood substance. The weakly acid solutions leaving the cation exchanger were passed through a second anion exchange filter and finally through a second decolorization filter. In this way, water-clear sugar solutions were obtained, which were completely free from acids and salts. Said solutions were concentrated to syrups of about 80 per cent sugar content. The syrups had the following composition (based on the material in the dry state).

	Syrup from Prehydrolysis	Syrup from Main Hydrolysis
	Per cent	Per cent
Glucose	25.6	82.5
Polymeric sugars	5.0	3.0
Galactose	5.3	1.1
Mannose	29.0	6.4
Arabinose	4.6	1.2
Xylose	30.5	5.8

After more than 80 per cent of the glucose had been crystallized out from the main hydrolysis syrup, the mother liquor was combined with the prehydrolysis syrup to a solution of the following composition:

	Per cent
Glucose	27
Polymeric sugars	7
Galactose	5
Mannose	22
Arabinose	4
Xylose	35

The neutral solution of said sugar mixture was adjusted to a total sugar content of about 40 per cent and converted to polyhydric alcohols with hydrogen under a pressure of 300 atm at a temperature which has allowed to rise slowly from about 70°C to about 120°C. A catalyst consisting of 80 % of SiO_2, 14 % of Ni, 5 % of Cu, .5 % of Mn and .5 % of Cr was used, and the reaction was continued until the absorption of hydrogen had essentially terminated.

The hydrogenated mixture, which may still contain a small

residual sugar content of about 1 to 3 per cent was separated from the catalyst and subjected to vacuum distillation whereby substantially the entire xylitol formed from xylose was distilled over. It was separated from the carrier steam by fractionated condensation, whereby it was obtained in excellent purity. The yield was 30 to 33 per cent, calculated on the total initial sugar input.

The darkish distillation residue was diluted with water to about 30 % and purified by percolation with a decolorizing resin. After concentration of the thus obtained clear solution to a solids content of about 75 %, mannitol crystallized out on cooling after seeding and could be separated, for instance by filtration. The yield was about 18 to 20 per cent, calculated on the total sugar input.

The mother liquor from the mannitol crystallization was percolated again over a decolorizing resin to remove the discoloring impurities, and then concentrated to a syrup consistency of about 75 to 80 per cent of solids content. The dry substance of said syrup comprised about 75 per cent of sorbitol in addition to other polyhydric alcohols. This syrup could be stored without precipitation of crystals for unlimited periods of time when about 25 per cent, calculated on the weight of the syrup, of xylitol were added.

EXAMPLE 2

1,000 kg of beech wood were comminuted to an average grain size of about 1 mm and hydrolyzed with 30 % HCl at 20°C, whereby 220 kg of hemicelluloses were dissolved (prehydrolysis). Subsequently, 430 kg of cellulose were dissolved out by means

of 40 to 41 % HCl at the same temperature (main hydrolysis). The solutions were separately concentrated to syrups by vacuum distillation, and processed as described in Example 1. The final syrups had the following composition, (based on the material in the dry state).

	Prehydrolysis Syrup	Main hydrolysis Syrup
	Per cent	Per cent
Glucose	4.9	87.3
Polymeric sugars	4.0	4.0
Galactose	1.0	0.5
Mannose	1.4	5.0
Arabinose	2.7	-
Xylose	86.0	3.2

After more than 60 per cent of the glucose had been crystallized out from the main hydrolysis syrup, the mother liquor and the prehydrolysis syrup were processed in the manner set forth in Example 1. The dry substance of the mother liquor had the following composition:

Glucose	54.4 %
Polymeric sugars	14.4 %
Galactose	1.8 %
Mannose	18.0 %
Arabinose	---
Xylose	11.4 %

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for producing pentitols and hexitols from wood, comprising hydrolyzing wood at temperatures of about 15 to 30°C first with about 29 - 37 % hydrochloric acid and then with 39 to 42 % hydrochloric acid, thereby obtaining substantially mixtures of pentoses in said first and mixtures of hexoses in said second hydrolysis step, recovering crystalline glucose from said mixtures of hexoses, treating the remaining hexose solution and said pentoses at elevated pressures and temperatures with hydrogen in the presence of a hydrogenation catalyst, separating xylitol from the hydrogenated product by steam distillation under reduced pressure, diluting the distillation residue in water, precipitating mannitol crystals in said solution, separating said crystallized mannitol from the solution, and concentrating said solution to a syrup consisting substantially of sorbitol.